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Measurement of atmospheric composition by the ATMOS instrument from Table Mountain Observatory

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ABSTRACT

Following its first flight on board the Space Shuttle "Challenger" as part of the Spacelab 3 payload, the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument has been operated at the Jet Propulsion Laboratory's Table Mountain Observatory (TMO; 34.4°N, 117.7°W, 2.23 km altitude) in the San Gabriel Mountains of Southern California. With the delay in the resumption of regular Shuttle flights, ATMOS has acquired a large number of high-quality, high-resolution infrared solar absorption spectra, spanning a period between late-1985 and mid-1990. These spectra are being analyzed to derive the column abundances of several atmospheric species including O_3, $HC\ell$, HF, and HNO_3. Although limited in temporal coverage, the preliminary results for these gases are discussed here in the context of the requirement and contribution to be made by similar instruments in detecting long term changes in stratospheric composition.

1. INTRODUCTION

The Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument is a Fourier transform infrared spectrometer (FTIR) designed to obtain vertical profile information on the abundance and composition of the middle atmosphere from a shuttle-based platform[1,2]. It operates on-orbit in the solar occultation mode, recording infrared solar absorption spectra at successive zenith angles through the Earth's atmosphere, from which vertical profile information can be inferred for many atmospheric constituents. Data obtained between April, 30 and May 1, 1985 by ATMOS during the Spacelab 3 mission have been successfully analyzed for the profiles of some thirty different tropospheric and stratospheric species (see refs. 2-6, and other references therein).

In this report, however, preliminary results are given for the column abundances of O_3, $HC\ell$, HF, and HNO_3 derived from data obtained at Table Mountain Observatory (34.4°N, 117.7°W), where the ATMOS instrument has been operated since the Spacelab 3 mission. These gases are among the key species to be monitored for evidence of secular changes in the chemical composition of the stratosphere. The accuracy with which these gases can be measured by this technique and the utility of TMO as a possible site for such measurements will be discussed with reference to the present results.

2. OBSERVATIONAL DATA SET

Following its return from the Spacelab 3 mission in late 1985, the ATMOS instrument was moved to TMO to test its performance before an expected shuttle reflight. Although routine engineering tests could be made at the Jet Propulsion Laboratory, it was desirable to obtain useful scientific data while verifying the instrument's integrity. Table Mountain Observatory provides an easily accessible site, with suitable facilities to make routine measurements by several instruments. For infrared solar absorption measurements, the site altitude of 2.23 km reduces the interference by tropospheric H_2O, CH_4 and CO_2, evident at the lower altitude of the San Gabriel Valley, and has a climate favorable to observation for some 300 days in a year.

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The first observation day for ATMOS at TMO was in October 1985. When the Challenger accident led to the suspension of shuttle flights, increased priority was given to measurements from TMO. Beginning December 1986, data were obtained as frequently as circumstances permitted. A series of observations from 44 separate days, spanning October 1985 to September 1989 have been assembled with the goal of studying seasonal and possibly secular variations.

The ATMOS instrument performance has been described elsewhere[1,2] but some characteristics are worth noting. The instrument produces a one million point double-sided interferogram every 2.2 seconds, which is transformed into a spectrum with a maximum resolution of 0.01 cm^{-1}. One of eight optical filters, each with a different bandpass in the 2 - 16 μm wavelength range of the HgCdTe detector response, was selected for each run. The signal-to-noise ratio (S/N) of a single spectrum obtained in this way ranged from 350 to 100:1, depending on the optical filter, but generally increasing with wavelength. For these ground-based observations, data were acquired with each optical filter for a period up to several minutes. This was sufficient time to record tens of individual spectra which, when averaged together, produced a spectrum with a S/N ratio of at least 1000 to one.

For most days, data were recorded at about 1, 5 and 10 airmasses, between sunrise and about 11:30 AM local time, and corresponding to solar zenith angles ranging from 89° to 12°. Data were not taken in the afternoon, when smog from the Los Angeles basin was often transported over TMO. This smog did not significantly interfere with measurements during the early morning as was verified from local measurements of tropospheric O_3[7]. These showed an increased amount of tropospheric ozone beginning in the late morning, due to Los Angeles basin area pollution spilling over the intervening San Gabriel Mountains and thence over TMO. However, this corresponded to the period of measurement of minimum airmass spectra when the slant paths through the lower regions of the troposphere were comparatively short. Thus tropospheric effects were minimized for observations of stratospheric gases.

3. DATA ANALYSIS

The analysis software used to retrieve the column abundances reported here has been described by Norton and Rinsland[8] and by Farmer[1], and used extensively for the analysis of ATMOS Spacelab 3 data and JPL Mk. IV interferometer data obtained from the NOZE 1[9,10], AAOE[11], and AASE[12] polar ozone campaigns. Retrieval procedures involved calculating synthetic spectra for small spectral intervals containing the absorption features of the target gas of interest, and scaling an assumed volume mixing ratio (VMR) -height profile until a best fit, in a least squares manner, was achieved between observed and calculated spectra. Constituent and physical parameter profiles were mapped on to a 150 km high model atmosphere separated into homogeneous 1 km layers.

Daily pressure-temperature profiles were constructed from National Meteorological Center (NMC) data sets[13]. Above the range of the NMC profiles (0.4 mb), the U.S. Standard atmosphere[14] was assumed, and the profile as a whole was then adjusted to be in hydrostatic equilibrium. The spectral line parameters used in this analysis were taken from the ATMOS molecular line parameter data base, described by Brown et al[15]. Parameters updated since this description will be noted below.

4. RESULTS AND DISCUSSION

a. Ozone

There has been significant effort to understand how stratospheric ozone may be evolving. This has led to a regular series of evaluations of the accuracy and reliability of current databases of O_3 measurements. Several exercises have been carried out to compare observational results and to improve the accuracy of retrieval schemes[16,17]. The high confidence in O_3 measurements can in part be carried forward to FTIR measurements of other gases. Validation of the FTIR measurements of O_3 by comparison to results from established techniques provides support for the accuracy of the reported values of these other stratospheric

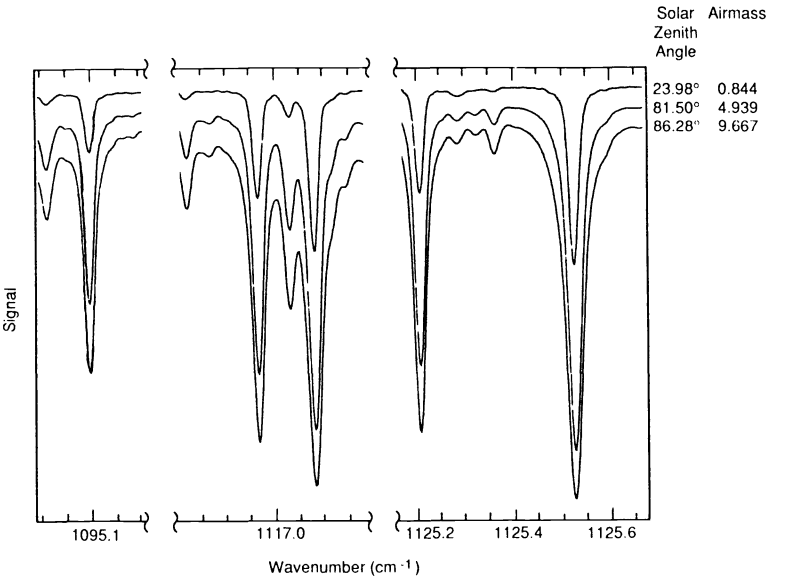

Figure 1. Three spectral intervals used in retrieving O_3 column abundances. These represent intervals from three spectra, shown offset from one another, all recorded on August 26th, 1987, at the zenith angles and airmasses indicated in the upper right hand corner. Line parameters for the strongest lines are given in Table 1. Note: the smaller scale divisions on the abscissa axis are every 0.05 cm^{-1}.

gases. Most of the discussion that follows will focus on a comparison of the present results with Total Ozone Mapping Spectrometer (TOMS) total ozone values, which have been extensively analyzed (see 16,18 and references therein). While the TOMS values are gridded to a much lower spatial resolution, 1° latitude by 1.25° longitude, they provide a complete temporal record and a broad basis for comparison with ATMOS/TMO results.

The ATMOS/TMO O_3 column abundances were determined from fits to spectral intervals selected primarily to contain O_3 absorption features which could be demonstrated to be relatively insensitive to pressure-temperature profile errors. Generally, these intervals contain transitions from lower state energy levels, E", in the range of 100 to 500 cm^{-1}. Further criteria required that the absorption lines were not strongly blended with those of other gases nor appeared completely opaque at their line center. Three windows (Figure 1) were selected on which to base the routine analysis. The spectral parameters for these lines are shown in Table 1, and are part of the ν_1 band, except for the feature at 1094.8 cm^{-1}, which is part of the ν_3 band. The line strength parameters are those of Flaud et al.[19]; the uncertainties in these parameters are the principal limitation on the retrieval accuracy for O_3 column abundances, and are given an estimated accuracy of ±10%.

For O_3, the *a priori* VMR profiles used in this analysis were calculated as month-by-month averages of the O_3 profiles measured by the JPL lidar system from TMO between 1987 and 1990 (see 20). These lidar results, which are determined as vertical concentration profiles, were converted to VMR profiles using NMC pressure-temperature data averaged on a month-by-month basis, taken from 1979-1990. Below the lower observational range of the lidar (about 15 km), an O_3 concentration of 1×10^{12} molecules cm^{-3} was assumed, a value slightly larger than that reported for tropospheric heights by a range of instruments during the Stratospheric Ozone Intercomparison Campaign (STOIC) held at TMO[21] in July-August, 1989. Above the lidar's upper range (about 50 km), the Spacelab 3 profile was used[3]. VMR profiles are illustrated in Figure 2. Comparisons between the various monthly models reveal only small differences, and after accounting for seasonal differences, are in good agreement with the ATMOS/SL3 O_3 vertical profile reported for 30°N. As might be expected, trial retrievals of total O_3 column abundance, using a variety of different *a priori* profiles, showed little sensitivity in the quality of the fit as to the exact vertical distribution of O_3 assumed. Only changes in the vertical profile that affected the relative distribution of O_3 on a scale height resolution appeared important. This is a function of the spectral resolution achieved in the ATMOS data, which does not fully resolve the exact pressure-broadened line shape under stratospheric conditions.

Given that the long-term trend in stratospheric O_3 at low to mid-latitudes is rather small, the ATMOS/TMO results are first plotted by day of the year to establish a seasonal climatology for column O_3

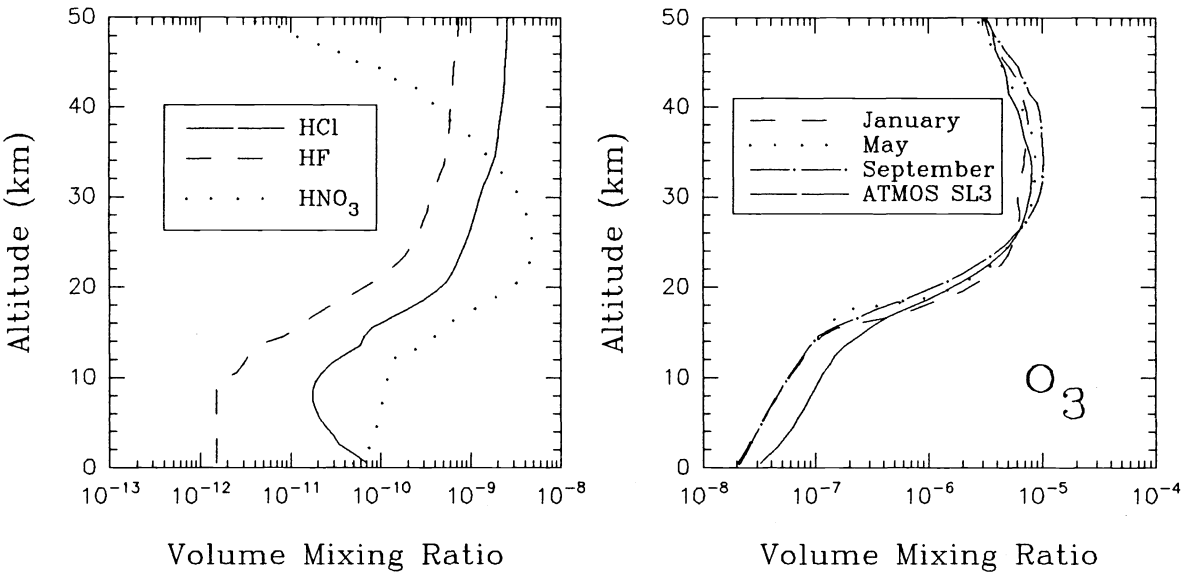

Figure 2. A priori *volume mixing ratio (VMR) profiles used for analyses. The left panel illustrates the VMR profiles for HCl, HF, and HNO_3. The profiles shown on the left have not been vertically shifted to account for changes in the tropopause altitude (see text for discussion). The right panel illustrates sample O_3 profiles, here, those for January, May and September. The ATMOS Spacelab 3 O_3 zonal average for 30°N is shown for comparison. The VMR profiles up to 50 km only are illustrated.*

measurements (Figure 3). The seasonal variation appears to be almost sinusoidal, with a peak-to-peak difference of 2.5×10^{18} molec.cm^{-2} and a mean summer column of 8×10^{18} molec.cm^{-2}. Significant variability and much larger column values are apparent in the first half of the year than in the second half. This is not inconsistent in appearance or on the average with TOMS values (version 6 processing results, interpolated from the gridded values to TMO location). When the day-by-day differences are plotted (Figure 3), significant departures can be seen, again in the first part of each year. The larger differences, increased variability, and higher column abundances can be partially attributed to advection of stratospheric air parcels from higher latitudes in the winter season through planetary wave activity. These air parcels, which may have higher levels of O_3, can be expected to have a small spatial extent, and to have a short residence time over TMO before being dispersed elsewhere. This phenomenon has been reported by McGee et al. from lidar O_3 profile observations over TMO[22] in October-November, but in this instance they noted a decrease in O_3 in the advected sub-polar air mass.

The good agreement, ±5% RMS, between ATMOS/TMO and TOMS total ozone in the later part of the year (day of year ≥ 181) provides some measure of confidence in the chosen analysis procedure, and is commensurate with the estimated precision (based on random error sources) of the ATMOS/TMO measurements. The accuracy of the results, based on the systematic errors, appears to be better than the estimated 10%. Table 2 summarizes the estimated error contributions from sources for all the gases discussed in this paper. The error sources are divided into random and systematic (the latter being just the spectroscopic parameter errors), with a root-sum-of-squares calculated from the two groups.

b. Hydrogen Chloride and Hydrogen Fluoride

Infrared solar absorption techniques offer one of the few means to measure these atmospheric constituents. As the primary sinks of Cl and F in the stratosphere, measurements of HCℓ together with HF are important indicators of the rate at which organic halocarbons are being destroyed and removed. The recent rapid increase in use and production of halocarbons has produced a reported increase in HCℓ and HF column abundances over the past decade[23,24].

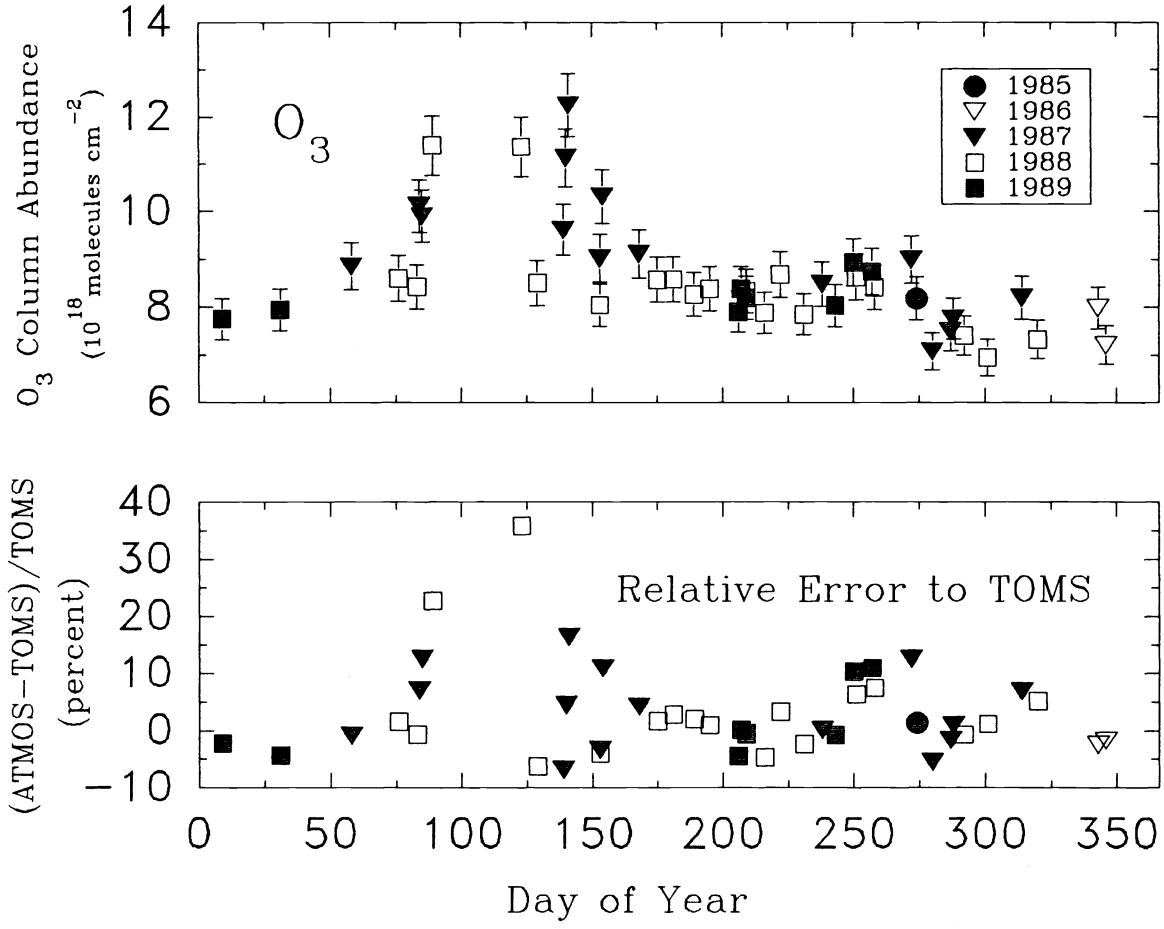

Figure 3. The upper panel shows the O_3 column abundances derived from the ATMOS/TMO data for the period of observation. The results are plotted as a function of day number of year to highlight seasonal variations. The lower panel indicates the relative difference between these values and the gridded TOMS total O_3 column abundance (version 6 processing) for the same days.

This present analysis for HCℓ was based on the P5 and R1 lines of the (1-0) band of $H^{35}C\ell$, centered at 2775.7610 cm^{-1} and 2925.8970 cm^{-1} respectively. To gain a better fit for the P5 line, a weak, neighboring O_3 line at 2775.84 cm^{-1} was fitted before the retrieval for HCℓ was attempted. Other lines were either too weak or blended with stronger absorption features of other gases. The spectral line parameters (Table 1) are the same as those used by Zander et al.[5] in analyzing ATMOS/SL3 data, Rinsland et al.[25] for ground-based measurements from Kitt Peak National Observatory, Arizona (31.9°N), and Zander et al.[23] for measurements from the International Science Station of the Jungfraujoch (ISSJ) in Switzerland at a latitude of 46.5°N. The vertical profile of HCℓ reported by Zander et al.[5], and based on the analysis of ATMOS/SL-3 observations made around 30°N, was chosen as the *a priori* profile to be scaled in the fitting to ATMOS/TMO observations.

Within the spectral range of the ATMOS instrument, only the R1 line of the 1-0 band of HF could be examined, all other lines being too weak or obscured by other gases. This line is made more difficult to analyze as it lies on the shoulder of a strong water line centered at 4039.235 cm^{-1}. This feature had to be carefully prefitted before the HF retrieval could be attempted. As with HCℓ, the assumed profile was taken from Zander et al[5]. and the same line parameters have been employed.

Table 1: Spectral Intervals Used for Analyses

Molecule	Interval Center (cm^{-1})	Interval Width (cm^{-1})	Line Center (cm^{-1})	Line Strength (molecule^{-1} cm^{-1})	Ground State Energy (cm^{-1})	Refs
O_3	1095.12	0.30	1095.0146 1095.1008	8.63×10^{-21} 5.19×10^{-22}	505.5065 310.2947	19
	1117.02	0.30	1116.9673 1117.0308 1117.0834	9.74×10^{-22} 1.21×10^{-22} 1.65×10^{-21}	205.6354 158.1653 127.2639	
	1125.36	0.50	1125.2086 1125.5243	9.12×10^{-22} 2.08×10^{-23}	183.4037 286.5665	
HCl	2775.78	0.15	2775.7610	2.88×10^{-19}	312.7310	29,30
	2925.90	0.10	2925.8970	4.20×10^{-19}	20.8780	
HF	4038.95	0.50	4038.9625	2.37×10^{-18}	41.1110	29,30
HNO_3	868.10	2.10	5 P-branch Manifolds	6.85×10^{-19} (Integrated Band Strength)	approx. 85 - 650	15

Note: Interval width was sometimes varied to achieve an improved fit by better determination of the baseline.

Table 2: Error sources and resulting percentage uncertainties in retrieved column abundances

Random Error Source	**O_3**	**HCl**	**HF**	**HNO_3**
Finite signal-to-noise	0.5	0.5	0.5	0.5
Error in 100% transmission level	2	2	2	2
Error in pressure-temperature profile	3	5	5	3
Error in fitting interfering lines	1	1	3	0.5
Error in assumed height registration	5	5	5	5
RSS total of random error	5.5	7.5	8	6.5
Systematic error from uncertainty in line parameters	10	5	5	10

In an effort to better model the seasonal variation of the height registration of HCℓ, HF, and HNO_3 in the stratosphere, the *a priori* profiles were vertically "shifted" up or down according to the difference in altitude of the concentration maxima of the monthly O_3 profiles and the ATMOS/SL3 30°N profile. For example, the maximum concentration of O_3 in the March profile was at ~22.5 km, while the SL3 maximum was at ~24.5 km. Therefore, in retrievals for the month of March, the profiles of the SL3 HCℓ, HF, and HNO_3 were shifted down 2 km.

The derived HCℓ and HF column abundances are plotted in Figure 4, together with the HF/HCℓ ratio as a function of time. The mean HCℓ column abundance for the period of measurement 2.6×10^{15} molec.cm^{-2}

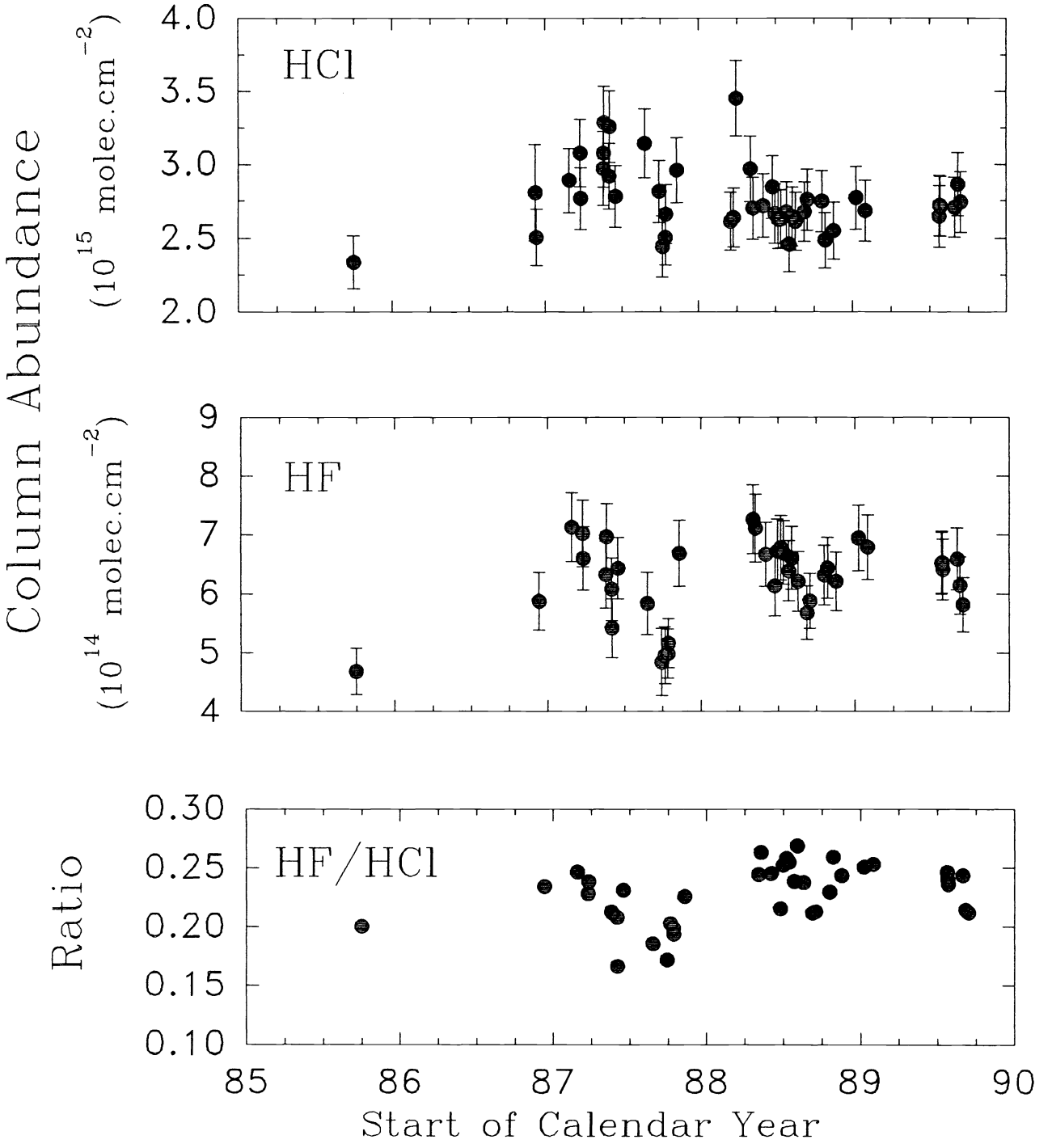

Figure 4. The retrieved HCl (upper) and HF (middle) column abundances from the ATMOS/TMO data set, plotted by year. The lower panel shows the HF/HCl ratio as determined from these values.

is in good agreement with measured columns from Kitt Peak and ISSJ; however, the HF column amounts of 6×10^{14} molec.cm^{-2} for ATMOS/TMO are lower by 2×10^{14} molec.cm^{-2} than the typical values from the ISSJ for the same period, but comparable to the values inferred for HF at Kitt Peak.

The resulting HF/HCℓ ratio calculated from the present ATMOS/TMO observations, around 0.23, is thus lower than that derived from the ISSJ measurements. The larger percent increase per year in HF, discernable in ISSJ and Kitt Peak observations, is not reproduced in the ATMOS/TMO data, almost certainly a result of the limited temporal coverage of the ATMOS/TMO observations. However, as a whole these measurements are consistent; there is very good agreement in measured columns from Kitt Peak and TMO, representing 32-34°N, but the HF column abundances are quite different from those obtained at the more northerly ISSJ. This significant latitudinal gradient in the HF column abundances is supported by the measurements made, for example, from aircraft flights over a range of latitudes during the Antarctic Airborne Ozone Experiment[11,26] and the Airborne Arctic Stratospheric Experiment[12].

c. Nitric Acid

Much of the current understanding of the distribution and behavior of HNO_3 is based on the measurements made by the Limb Infrared Monitor of the Stratosphere (LIMS) from the NIMBUS 7 satellite. These data showed that the sink of NO_x has its largest stratospheric level at higher latitudes, and builds up during the winter period[27]. Recently, ground-based FTIR measurements from both the ISSJ and Kitt Peak have been analyzed for the seasonal variations in HNO_3 and for any long term trends[28]. The limited number of measurements available showed no statistically significant long term trend between 1977 and 1990, and no seasonal variation at the latitude of Kitt Peak Observatory.

Five P-branch manifolds centered about 868.10 cm^{-1} were used for analysis, consistent with the approach by Rinsland et al.[28] for measurements of HNO_3 from Kitt Peak and the ISSJ. The ATMOS/SL3 30°N profile reported by Russell et al[6]. has been used as the *a priori* vertical distribution of HNO_3. The retrieved HNO_3 column abundances are shown in Figure 5 as a function of the day number of the year. The larger number of measurements obtained from TMO, compared to those analyzed by Rinsland et al. from Kitt Peak, do show a seasonal cycle similar to that derived by those authors from the ISSJ observations. Typical HNO_3 column abundances of 9×10^{16} molec.cm^{-2} have been derived for the summer, rising by as much as 50% in the winter period. As with the other gases, the values found during this period were highly variable.

5. CONCLUSIONS

Total column measurements of O_3, HCℓ, HF, and HNO_3, have been made between December, 1985 and September 1989 from the Table Mountain Observatory. These results, when compared to similar measurements from the ISSJ and Kitt Peak for the acid species, and to gridded TOMS total ozone columns, are in good agreement. Significant seasonal variations can be seen for all of these gases, with large variability and indeed higher column abundances observed in the first half of each year. These larger columns are probably indications of the transport of high latitude stratospheric air with enhanced levels of these gases down to the latitude of observations at TMO. The comparison of TOMS total O_3 column with the individual results from ATMOS/TMO show very good agreement to ±5% for the latter part of the year, but the larger differences noted in the winter (with most showing the ATMOS/TMO values being larger than TOMS), suggests that the spatial extent of these air parcels is small in comparison to the spatial resolution of the gridded TOMS data. For TOMS observations, these small air parcels enriched with O_3 would appear to be diluted against the larger background of the normal mid-latitude O_3 levels.

A comparison of the measurements between the two years 1987 and 1988 indicate marked differences in variability or scatter of measured columns (Figure 6). The column abundances measured throughout 1987 were more variable, with generally higher than expected columns abundances. For HF, where a large secular trend of around 10% per year has been previously observed, these higher column abundances through 1987 damp out any interannual trend from 1987 to 1988. This is also corroborated by the HNO_3 column abundances

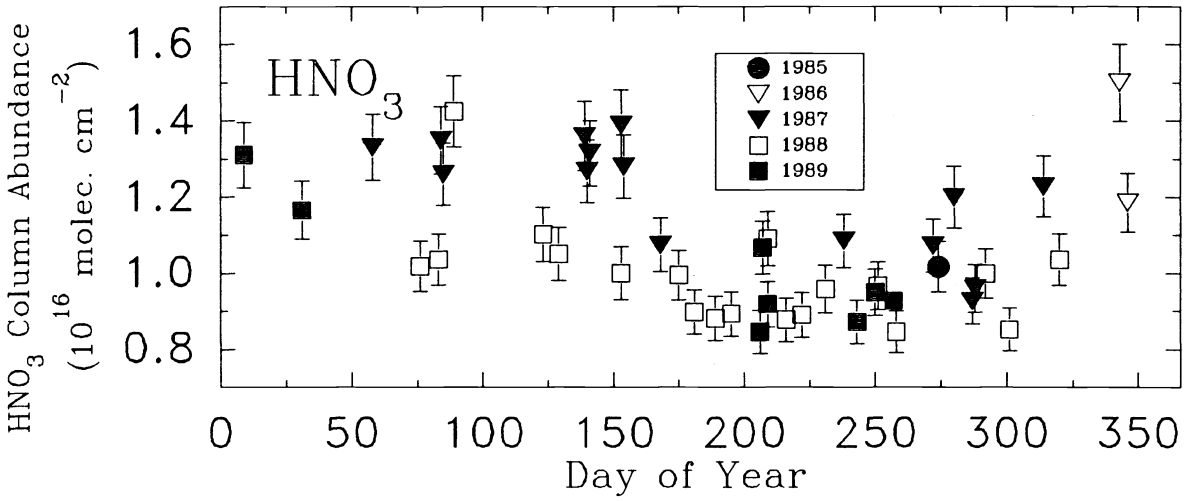

Figure 5. The retrieved HNO_3 column abundances from the ATMOS/TMO observations, plotted as function of day of the year to highlight seasonal variations.

for the same period; with no long term trend expected, the difference between these years shows a drop in the mean HNO_3 level of more than 10%. The statistical significance of this and further corroborative data is being investigated. In isolation, the ATMOS/TMO observations are difficult to interpret for any useful trend data in these gases, but they can be used to support similar measurements made at other sites, particularly where there is a suitable overlap in latitude as found in measurements from Kitt Peak.

Infrared solar absorption measurements, and the ATMOS instrumental approach in particular, provide a powerful means of measuring $HC\ell$, HF and HNO_3 simultaneously. However, high resolution is required (better than 0.01 cm^{-1}), particularly for analyzing HF. A regular and consistent program of measurements by FTIRs, made at a frequency of observation of once per week, can provide reliable information on secular trends when suitable account can be made statistically for the short term variations observed. The cloud cover and climatic conditions encountered at the Table Mountain Observatory provides observation opportunities on some 300 days each year, sufficient for almost year-round observation. However, because of TMO's proximity to Los Angeles, solar absorption measurements like those described here should only be attempted in the morning to avoid the effects of the afternoon smog. As the ATMOS experiment is now preparing for flight on future Space Shuttle missions, there are no immediate plans to extend this current data base, but it could still provide an important basis, in conjunction with any future ground-based measurements from TMO, for the determination of secular trends.

The analysis of the current data set will be continued to derive column abundances of other trace species. The uncertainty in the tropospheric contribution to the measured column abundance of stratospheric gases will also be investigated to gain improved accuracy and a better understanding of the changing composition of the stratosphere.

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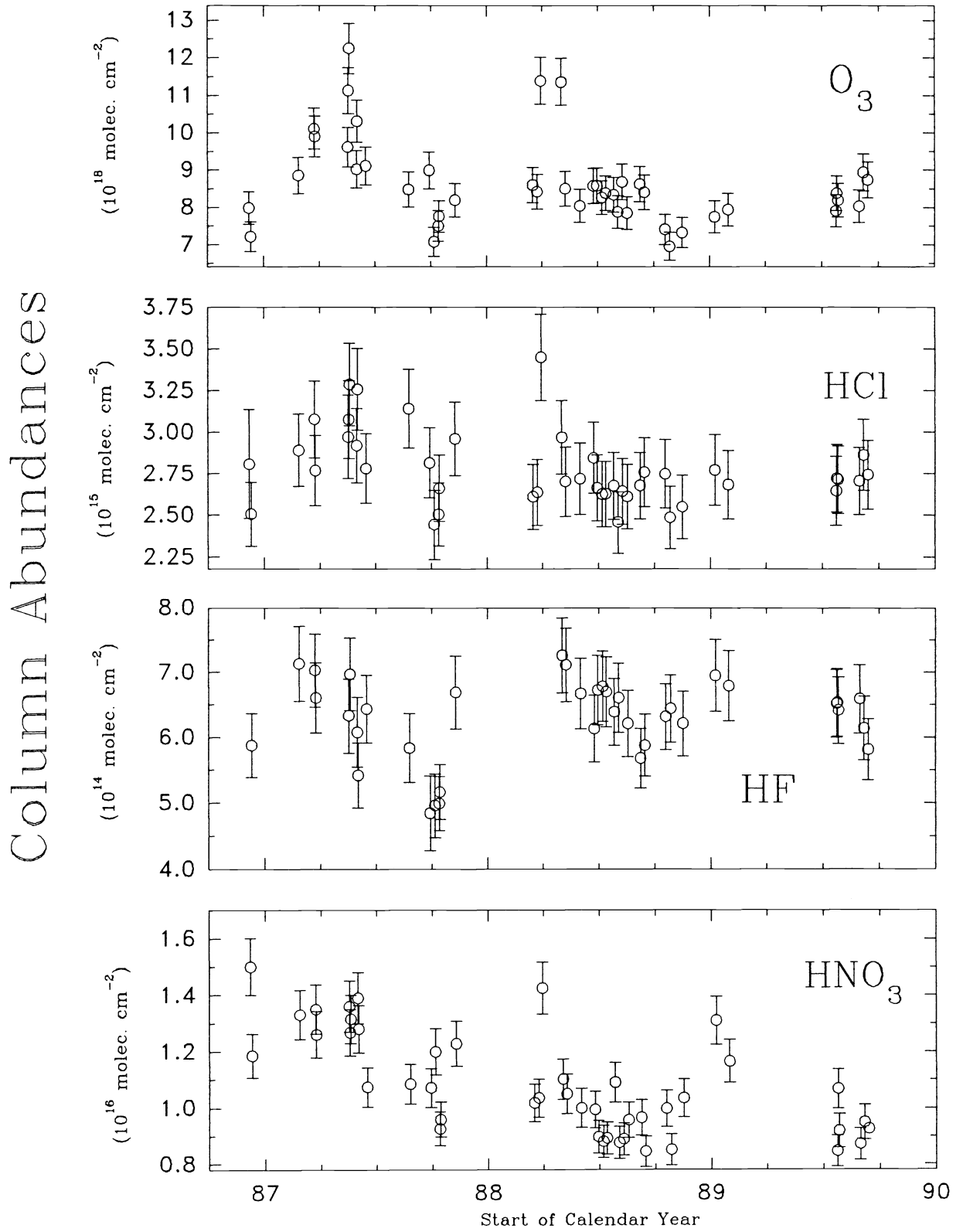

Figure 6. A composite of the retrieved column abundances of O_3, HCl, HF, and HNO_3 in chronological order of the date of measurement.

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